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Citation: The Journal of Chemical Physics **42**, 2232 (1965); doi: 10.1063/1.1696272
View online: http://dx.doi.org/10.1063/1.1696272
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/42/6?ver=pdfcov
Published by the AIP Publishing

Explanation of Some Differences in the Correlation Energies of CH_4, Ne, and NH_4^+

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(Received 29 October 1964)

The most recent nonempirical value for the correlation energy of CH_4, $E_{corr}(CH_4)$, is -0.344 a.u. Prior to this, E_{corr} of the isoelectronic systems Ne and CH_4 had been assumed equal (-0.393 a.u.). This paper gives a simple explanation of 50% of this difference, that is, from electrostatics the four protons in CH_4 smeared over a sphere (spherical model) and only six at the center exert a smaller potential than all 10 at the center do in neon. This leads to a much larger effective nuclear charge for the orbitals in Ne. The Z dependence of E_{corr} of Ne-like ions then sets $|E_{corr}(CH_4)|$ at 0.025 a.u. less than $|E_{corr}(Ne)|$. This approach will be useful in relating molecular E_{corr}'s to the correlation energy of related and better-understood atomic systems and in locating molecular Hartree–Fock limits. Two other results in this paper are (a) $E_{corr}(NH_4^+)$ given as -0.330 a.u. is too low and should be at least 0.344 a.u., that is, $E_{corr}(CH_4)$. This suggests a better choice for the proton affinity of NH_3. (b) $|E_{corr}(SiH_4)|$ will be about 0.08 a.u. less than $|E_{corr}(\text{argon})|$.

INTRODUCTION

RECENTLY, Krauss[1] found the correlation energies of CH_4 and NH_4^+ to be -0.344 and -0.330 a.u.,[2] respectively. His Hartree–Fock calculations used a basis set of 19 Gaussian-type functions, $f(x, y, z)\exp(-ar^2)$. Prior to these results it had been assumed that the molecular correlation energy of CH_4 could not be very different from -0.393 a.u. of the isoelectronic system, Ne. Why were the correlation energies of CH_4 and Ne expected to be equal? Simply because they are isoelectronic, have the same total nuclear charge, and the neonlike spherical approximation to CH_4 gives a fairly good Hartree–Fock energy.

This paper shows that about 50% of this difference in correlation energies between CH_4 and neon has a simple explanation. Neon and the spherical approximation to CH_4 have a ^1S wavefunction ($1s^2\ 2s^2\ 2p^6$) and a total nuclear charge of $Z=10$. But the $2s$ and $2p$ orbitals in Ne see a much larger effective nuclear charge; that is, $Z_{eff}(Ne)\simeq 6$, $Z_{eff}(CH_4)\simeq 2.5$. This difference comes from having 4 of the 10 protons of CH_4 smeared out on a sphere of radius 2 a.u. and not all at the center as in Ne. From electrostatics, an electron inside of this sphere sees a constant potential but, were these four protons at the center, an electron would see a potential $=4/r_i$ where $r_i<2.067$ a.u.—hence the larger effective nuclear charge in Ne. From the Z dependence of the correlation energies of Ne-like ions, this difference of 3.5 a.u. in the effective nuclear charge of the $2s$ and $2p$ orbitals in Ne and CH_4 sets $|E_{corr}(CH_4)|$ at 0.025 a.u. less than $|E_{corr}(Ne)|$. We[3] have recently shown that there is no strongly Z-dependent pair-correlation energy in Ne-like ions, and hence this analysis does not depend critically on exact changes in the Z dependence of orbitals going from CH_4 to Ne.

Such theoretical understandings of correlation energies in simple atomic systems can give estimates of the correlation energy in related molecular systems. This will then be helpful in locating the Hartree–Fock limit from a series of approximate molecular Hartree–Focks. For example, this Z effect puts the correlation energy of SiH_4 at 3 eV less than that of its united atom, argon. This will be useful when good Hartree–Focks for SiH_4 become available. Krauss[1] tentatively gives $E_{corr}(NH_4^+)=0.330$ a.u. A similar comparison between NH_4^+ and CH_4 suggests: (a) $E_{corr}(NH_4^+)$ should be at least as large as in CH_4, that is, 0.344 a.u. and, consequently, (b) the proton affinity of NH_3 chosen in Ref. 1 is too low. This can be of some help in selecting the best value from the literature[4] for the proton affinity of NH_3.

Explanation of the remaining difference in E_{corr} of CH_4 and Ne may require a detailed analysis. As a reminder in any such analysis, we mention that the number of states resulting from a particular excited configuration in a configuration interaction (CI) study and mixing with the CH_4 ground state will be different if one starts from (a) the spherical approximation ^1S to the ground state or (b) the correct $^1\Gamma$ ground state[5] (in most cases more with the $^1\Gamma$ ground state). This can be seen by placing the particular excited state in an electrical field of tetrahedral symmetry.[5] This difference in the number of interacting configurations clearly is not sufficient to indicate that $|E_{corr}|$ of the real CH_4 molecule should have been expected to be larger

[1] M. Krauss, J. Chem. Phys. **38**, 564 (1963); see also B. J. Woznick, *ibid.* **40**, 2860 (1964).

[2] This value is tentative due to the uncertainty in the proton effinity of NH_3; see Ref. 1.

[3] This concerns $2s^2$ correlation, $\epsilon(2s^2)$. In Neon $\epsilon(2s^2)\approx -0.3$ eV and almost Z independent: V. McKoy and O. Sinanoğlu, J. Chem. Phys. **41**, 2689 (1964). Compare with $\epsilon(2s^2)\simeq -3.2$ eV and large Z dependence $\Delta\epsilon(2s^2)/\Delta Z\approx 0.013$: L. C. Allen, E. Clementi, and H. Gladney, Rev. Mod. Phys. **35**, 465 (1963).

[4] Values range from 0.277 to 0.318 a.u. See, for example, F. W. Lampe and F. Field, Tetrahedron **7**, 189 (1959).

[5] $^1\Gamma$: notation for ground state of CH_4. See, for example, J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Company, Inc., New York, 1963), Vol. 1.

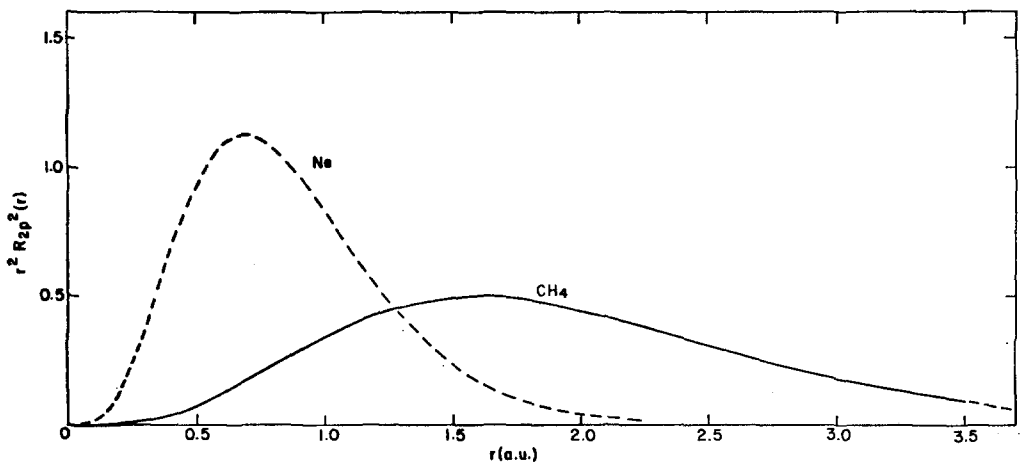

FIG. 1. Comparison of $r^2R_{2p}^2(r)$ in Ne and CH_4 (spherical model): - - - - Ne ($\gamma=2.879$); —— CH_4 ($\gamma=1.26$), see Eq. (2).

than $|E_{corr}(NE)|$. It does mean that the CI expansion for $CH_4(^1S)$ will not only contain different matrix elements and excitation energies from the CI expansion of $CH_4(^1\Gamma)$ but that also the total number of configurations in the two CI expansions will be different. How this affects the final result will depend on all these three differences. This should be kept in mind in any CI study using the spherical approximation to $CH_4(^1\Gamma)$.

THEORY AND CH_4 RESULTS

The CH_4 molecule has the shape of a regular tetrahedron, the four protons each at a distance of 2.067 a.u. from the central carbon atom. The molecule belongs to the tetrahedral symmetry group T_d. The equilibrium configuration is $(1a_1)^2(2a_1)^2(2t_{2x})^2(2t_{2y})^2(2t_{2z})^2$, where a_1 and t_2 denote the two types of MO's corresponding to the irreducible representations A_1 and T_2 of the tetrahedral symmetry group. Expanding the potential due to the protons in harmonics centered on carbon and retaining only the first term in such an expansion, the molecule in its ground state has a spherically symmetrical electronic wavefunction (^1S). The Hartree–Fock (HF) wavefunction is, like that in neon,

$$\phi_0=A(1s^22s^22p_x^22p_y^22p_z^2). \quad (1)$$

This is the spherical approximation. With a single Slater orbital each for the 1s, 2s (orthogonalized to 1s), and 2p orbitals, Parr[6] obtained −39.473 a.u. (best HF = −40.167 a.u.[1]). A similar basis set in neon gives an energy of −127.812 a.u.[7] (best HF = −128.547 a.u.[8]). From the variational principle, the difference in the wavefunction, that is, between the "single Slater orbital" approximation and the best HF functions, will be larger than the corresponding energy difference, for example, 10%–15% difference in the 2p function of Ne. For our purpose, the approximate wavefunctions are good enough and physically give the effective nuclear charge. Later we look at the effect on the results of improving the wavefunction for CH_4 other than simply introducing more 2p-like functions. These turn out small.

Figure 1 shows the radial density of the 2p functions in Ne and CH_4 (spherical approximation)

$$R_{2p}=(2\gamma^{\frac{5}{2}}/\sqrt{3})re^{-\gamma r}. \quad (2)$$

For Ne $\gamma=2.879$[7] and CH_4 $\gamma=1.262$[6],

$$\gamma=\tfrac{1}{2}(Z-\sigma)=\tfrac{1}{2}Z_{eff}. \quad (3)$$

σ is the screening constant, Z the total nuclear charge (in an atom), and Z_{eff} the effective nuclear charge. Then Z_{eff} (2p or 2s)$\simeq$5.8 in Ne and about 2.5 a.u. in CH_4. The 2p electron in Ne sees a much larger effective nuclear charge than does the 2p electron in CH_4. Both systems have a total nuclear charge of 10, but in neon all are at the center and an electron sees a nuclear potential energy, $-10/r_i$. In CH_4 four of these are smeared out over the surface of a sphere (radius equal to C–H bond length), and only six are at the center. From classical electrostatics, an electron outside this sphere has the same nuclear potential as in Ne($-10/r_i$), but an electron inside this sphere sees a constant potential from the smeared-out electrons, that is, $-4/2.067$ which is less than $-4/r_i$ for $r_i<2.067$. Figure 2 shows that the electron spends a good bit of its time at $r<2.067$. This leads to a smaller effective nuclear charge for the 2p electron in CH_4. What effect does this difference in effective nuclear charge have on $E_{corr}(CH_4)-E_{corr}(Ne)$?

In the spherical approximation, CH_4 is a Ne-like ion. The correlation energy of Ne-like ions increases

[6] A. Saturno and R. Parr, J. Chem. Phys. **33**, 22 (1960).
[7] E. Clementi and D. L. Raimondi, J. Chem. Phys. **38**, 2686 (1963).
[8] E. Clementi, J. Chem. Phys. **38**, 996 (1963).

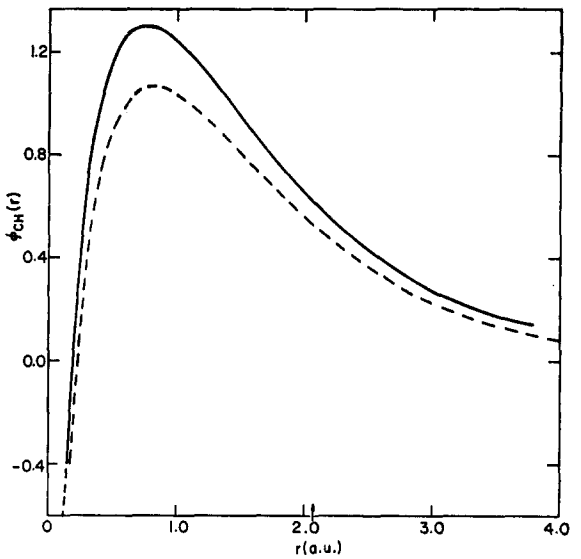

FIG. 2. Bond orbital in CH_4 plotted along direction of C–H bond: —— bond orbital built from sp^3 carbon hybrid and atomic orbital on hydrogen (Ref. 11); - - - - "one-center" bond orbital, that is, from one-center $2s$ and $2p$ orbitals (Ref. 6).

with increasing nuclear charge. The curve in Fig. 3 is a least-squares fit to Clementi's data.[9] From the slope of this curve, $\Delta E_{\text{corr}}/\Delta Z \simeq 0.0075$. In the "single Slater orbital" approximation,

$$\Delta Z \simeq \Delta Z_{\text{eff}}, \tag{4}$$

with σ constant in an isoelectronic series.

$$\Delta E_{\text{corr}}/\Delta Z \simeq \Delta E_{\text{corr}}/\Delta Z_{\text{eff}} \simeq 0.0075. \tag{5}$$

The $\Delta Z_{\text{eff}} \approx 3.3$, and ΔE_{corr} between Ne and CH_4 is 0.025 a.u. This ΔZ_{eff} of 3.3 is for the $2p$ orbital, but $\Delta Z_{\text{eff}}(2p) \simeq \Delta Z_{\text{eff}}(2s)$ and most of this Z dependence comes from $2p^6$ and $2s^2 \rightarrow 2p^6$ correlation.[10] The choice of ΔZ_{eff}, however, is not critical for there are no strongly Z-dependent pair energies in $1s^2\ 2s^2\ 2p^6$ systems.[3]

This simple analysis already explains 50% of the difference in E_{corr} between CH_4 and Ne. A more detailed analysis of this Z effect may give more of ΔE_{corr}, but is not worthwhile at this stage.

The curve of E_{corr} of Ne-like ions versus Z (Fig. 3) used in our extrapolation is quite reliable. Clementi[9] found $E_{\text{corr}}(F^-) = -0.398 \pm 0.003$ a.u. by extrapolation of his data for Ne-like ions. That $|E_{\text{corr}}(F^-)|$ comes out slightly larger than $|E_{\text{corr}}(\text{Ne})|$ ($Z=9$ and 10, respectively) is not significant. First the difference is quite small compared with differences we are concerned with, and the value of $E_{\text{corr}}(F^-)$ was not expected to be very accurate as shown by the uncertainty of 0.003 a.u. assigned to it. The linear increase in E_{corr} of the Ne-like ions with Z is quite reasonable. There is no degeneracy for infinite Z in Ne-like ions, but it is not necessary to have such a degeneracy in order to observe a Z dependence of E_{corr}. Such a degeneracy causes a large Z dependence. In general the various matrix elements of a CI study on such a series can increase such that E_{corr} increases with Z. This is well supported by (a) $2s$–$1s$ intershell correlation increases with Z[11] and (b) Donath's[12] CI study on F^-, Ne, Na^+ which gives about 68% of the total correlation energy, finds E_{corr} of F^-, Ne, Na^+ to be in the ratio 1:1.1:1.23.

We use the Z dependence of total E_{corr}. This Z dependence can certainly be regarded as the sum of Z dependence of all pair-correlation energies in the system. We do not make any assumptions about the Z dependence of any pair energy, but only that none is strongly Z dependent. Carlson[13] used atomic correlation data to estimate the correlation energy of CH_4, but took the empirically determined Z dependence of $2s^2$ correlation energy. To get this[9] various pair energies are assumed transferable from one system to another. We have shown that this neglects the exclusion effects of the many-electron theory[3] and incorrectly leads to a large Z dependence for $2s^2$ correlation in the first-row atoms. With the correct exclusion effects, the Z dependence of $2s^2$ correlation, for example, in Ne-like ions, is quite small. Linderberg and Shull's[14] predicted Z dependence for $2s^2$ correlation is for the Be-like ions and not for the neutral atoms of the first row.

EFFECT OF IMPROVING THE ORBITALS

So far we have used the simplest approximation to $\varphi(2t_{2x})$; that is, a single Slater orbital in the spherical approximation. It gives 98% of E_{HF}. How well do these orbitals compare with those that explicitly con-

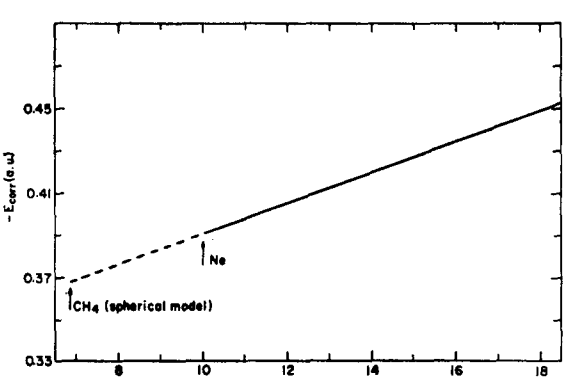

FIG. 3. Correlation energy of Ne-like ions (Ref. 9) vs Z showing E_{corr} of spherical model of methane.

[9] E. Clementi, J. Chem. Phys. **38**, 2248 (1963).

[10] In a single Slater orbital approximation $2s = A\, r \exp(-\alpha r) + B \exp(-\beta r)$. α is then only crudely an effective nuclear charge.

[11] C. S. Sharma and C. A. Coulson, Proc. Phys. Soc. (London) **80**, 81 (1962).

[12] W. E. Donath, J. Chem. Phys. **35**, 817 (1961).

[13] K. D. Carlson and P. N. Shancke, J. Chem. Phys. **40**, 613 (1964).

[14] J. Linderberg and H. Shull, J. Mol. Spectry. **5**, 1 (1960).

tain a contribution from orbitals centered on the protons? Such wavefunctions can better represent the orbitals in the vicinity of the protons. It is important that this improvement over the simple approximation is not large for the difference in Z_{eff} in CH_4 and Ne comes precisely from having four protons away from the center in CH_4.[15]

One such wavefunction is Oleari's[16] which builds up the total wavefunction from bond orbitals written as linear combinations of an sp^3 hybrid orbital of carbon and the 1s atomic orbital on hydrogen (energy$=-40.122$). Fig. 2 is a plot of this bond orbital along the C–H bond and also of the "one-center" bond orbital built up from Parr's orbitals.[6] The difference cannot affect our results substantially. In another LCAO–MO calculation on CH_4, Sinai[17a] only obtained an energy of -39.8 a.u. He used the free atom orbital exponents: $\gamma=1$ for H nucleus and γ (2s or 2p) on carbon$=1.625$, whereas Oleari[16] determined all orbital exponents variationally (except the 1s orbital exponent on carbon) and got $\gamma=0.41$ for H nucleus and γ (2s or 2p) $=1.45$. Oleari's value should then be clearly better than Sinai's.[17b]

OTHER XH_n SYSTEMS

Can this effect tell us anything about total E_{corr} in other XH_n molecules, for example, H_2O, HF, etc.? It may establish some trend, but differences between very similar molecules, for example, H_2O and HF, will be much smaller and less reliable. The effect can give useful results on NH_4^+ and SiH_4.

Krauss gives the correlation energy of NH_4^+ as -0.330 a.u. tentatively[1] [$E_{\text{corr}}(CH_4)=-0.344$ a.u.]. For NH_4^+ $Z_{\text{eff}}(2s)=4.34$, $Z_{\text{eff}}(2p)=3.24$,[18] and in CH_4 these are 2.94 and 2.5, respectively. We then expect $|E_{\text{corr}}(NH_4^+)|$ to be at least equal to $|E_{\text{corr}}(CH_4)|$ if not slightly larger. The experimental energy of NH_4^+ and consequently $E_{\text{corr}}(NH_4^+)$ is as uncertain as the proton affinity of NH_3.[1] Proton affinities range from 0.277 to 0.318 a.u.[19] Perhaps we should reconsider our choice of the proton affinity and the best value may well be larger than 0.277 a.u.[1]

A similar comparison can be made between the correlation energies of SiH_4 and argon. The correlation energy of argon is -0.79 a.u.[20] The difference in Z_{eff} between SiH_4 and argon[7,15] is about 2.5 to 3. The slope of the curve E_{corr} vs Z for argonlike ions[20] is very approximately 0.014. This sets the correlation of SiH_4 at about -0.75 a.u. In CH_4 we only got 50% of the total ΔE_{corr} for Ne and CH_4 so a better estimate of $E_{\text{corr}}(SiH_4)$ would be -0.71 a.u.

CONCLUSIONS

The correlation energies of CH_4 and Ne had been assumed equal simply because in the spherical approximation CH_4 has a neonlike configuration with the same total nuclear charge as Ne. Krauss'[1] Hartree–Fock on CH_4 unexpectedly gave $|E_{\text{corr}}(CH_4)|$ 0.05 a.u. less than $|E_{\text{corr}}(\text{Ne})|$. We show that 50% of this difference comes from the very different effective nuclear charges the 2s- and 2p-like orbitals seen in CH_4 and Ne. In CH_4, with four protons smeared over a sphere of radius 2.07 a.u. and only six at the center, classical electrostatics shows that the orbitals will have a smaller effective nuclear charge. The Z dependence of E_{corr} in Ne-like ions give $|E_{\text{corr}}(\text{Ne})| - |E_{\text{corr}}(CH_4)| \simeq 0.025$ a.u. (obs $\Delta E_{\text{corr}} \simeq 0.05$ a.u.).

Similar comparisons between some XH_n molecules and their united atoms allow us to compare the correlation energies of the two systems. Good Hartree–Focks for atomic systems are more available, and with such comparisons we can work back to estimate the molecular Hartree–Fock limit. Two related applications in this paper are: (a) $E_{\text{corr}}(SiH_4)$ will be about -0.71 a.u., but $E_{\text{corr}}(\text{Ar})$ -0.79 a.u.; (b) Krauss' estimate of $E_{\text{corr}}(NH_4^+)=-0.33$ a.u. seems too low. Comparison of Z_{eff} of orbitals in CH_4 and NH_4^+ indicates that at least $E_{\text{corr}}(NH_4^+) \simeq E_{\text{corr}}(CH_4)$ if not a little larger. Experimental uncertainties in the proton affinity of NH_3 may be responsible for Krauss' result: $|E_{\text{corr}}(NH_4^+)| < |E_{\text{corr}}(CH_4)|$.

[15] A better approximation to $\phi(2t_{2x})$ is $a^{\frac{1}{2}}\phi(2p_x)+b^{\frac{1}{2}}\phi(3d_{yz})$ still in the one-center expansion. But b/a is small (0.062), see C. Carter, Proc. Roy. Soc. (London) **A235**, 321 (1956).

[16] L. Oleari, Tetrahedron **17**, 171 (1962).

[17] (a) J. J. Sinai, J. Chem. Phys. **39**, 1575 (1963); (b) Russell Pitzer has kindly pointed out that the difference between the two approximations (0.32 a.u.), however, seems too large to be accounted for by Oleari's optimization of the orbital exponents. It may be due to Oleari's use of Mulliken's approximation on certain integrals or otherwise some numerical error.

[18] M. J. Bernal, Proc. Phys. Soc. (London) **A66**, 514 (1953).

[19] F. W. Lampe and F. Field, Tetrahedron **7**, 189 (1959).

[20] E. Clementi, J. Chem. Phys. **39**, 175 (1963).